Nd₂O₃ nanostructures: Simple synthesis, characterization and its photocatalytic degradation of methylene blue

Sahar Zinatloo-Ajabshir, Sobhan Mortazavi-Derazkola, Masoud Salavati-Niasari*

Institute of Nano Science and Nano Technology, University of Kashan, Kashan, P. O. Box. 87317-51167, I. R. Iran

* Corresponding author. Tel.: +98 31 55912383; Fax: +98 31 55913201; E-mail address: salavati@kashanu.ac.ir (M. Salavati-Niasari)

Abstract

Pure hexagonal Nd₂O₃ nanostructures have been synthesized via a simple precipitation way. For the first time, nanostructured Nd₂O₃ was produced with utilizing triethylenetetramine as a new precipitant and neodymium nitrate as a neodymium source. The analyses of XRD, FESEM, FT-IR, TEM, EDX, BET and DR-UV-vis were applied to characterize the as-prepared nanostructured Nd₂O₃. To evaluate the influence of various capping agents on the morphology, grain size and photocatalytic performance of Nd₂O₃, several experiments were performed. The results demonstrated that the kind of capping agent has substantial impact on the shape, grain size and photocatalytic performance of Nd₂O₃. In addition, application of the synthesized Nd₂O₃ samples as photocatalyst by photodegradation of methylene blue contaminant under ultraviolet illumination was investigated.

Keywords: Ceramic; Nd₂O₃; Nanostructures; Photocatalytic properties; Optical properties.

1. Introduction

...Rare earth metal oxides, particularly neodymium oxide (Nd₂O₃), have recently attracted enormous interest for application in catalysts, UV absorbent, luminescent materials, protective coatings and

magnets owing to their wonderful properties [1-8]. There are a variety of ways to synthesize Nd_2O_3 , including sol-gel, hydrogen plasma-metal reaction, precipitation, thermal decomposition and combustion [9-14]. The precipitation approach has been confirmed to be a simple and adaptable route to produce the materials and optimize their shape and grain size. The fundamental properties and uses of the materials depend on their grain size and shape. Following this issue, many research attempts have been devoted to the shape and size-controlled synthesis of materials [15-32].

Here, the nanostructured Nd_2O_3 has been produced via a simple precipitation way. For the first time, pure hexagonal Nd_2O_3 nanostructures were synthesized with utilizing triethylenetetramine as a new precipitant and neodymium nitrate as a neodymium source. The new precipitant (triethylenetetramine) with the great steric hindrance influence may play as co-capping agent role. In this investigation, the dependence of the shape, size and photocatalytic performance of Nd_2O_3 on the kind of capping agent was presented. The photocatalytic performance was examined via decompose of methylene blue pollutant under ultraviolet illumination.

2. Materials and methods

2.1. Materials and characterization

Triethylenetetramine, sodium dodecyl benzene sulfonate (SDBS), ethylenediamine, methanol, ethylenediaminetetraacetic acid disodium salt (Titriplex III), propandiamine, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 2-hydroxy-1-naphthaldehyde were purchased from Merck. Schiff base (bis-(2-hydroxy-1-naphthaldehyde)-propandiamine as capping agent has been prepared similar to previous route [12]. X-ray diffraction (XRD) patterns of the as-formed samples were recorded with employing a diffractometer of Philips Company with X'PertPromonochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). FESEM images of as-prepared Nd_2O_3 samples were visualized with a MIRA3 FEG-SEM. Fourier transform infrared

spectrum of the formed Nd_2O_3 sample was obtained on a Shimadzu Varian 4300 spectrophotometer in KBr pellets in the $400\text{--}4000\text{ cm}^{-1}$ range. The compositional analysis (EDS) of the as-formed Nd_2O_3 sample was done with a Philips XL30 microscope. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. The UV-vis diffuse reflectance spectrum of the as-synthesized nanostructured Nd_2O_3 sample was obtained on a UV-vis spectrophotometer (Shimadzu, UV-2550, Japan). Transmission electron microscope (TEM) micrographs of the obtained Nd_2O_3 sample were taken on a JEM-2100.

2.2. Synthesis of Nd_2O_3 nanostructures

Nd_2O_3 products have been synthesized via a simple precipitation way. At first, SDBS solution (stoichiometric amount of SDBS dissolved in distilled water) was added drop-wise into the neodymium nitrate solution (1 mmol of neodymium nitrate dissolved in distilled water) under magnetic stirring. After that, the pH of the resultant mixture was adjusted to 10 via drop-wise addition triethylenetetramine (precipitant) solution. Then, additional stirring was carried out for 1/6 h. The formed precipitate was separated through centrifugation, washed by distilled water and methanol, air-dried and at last calcined at $700\text{ }^\circ\text{C}$ for 2 h (sample no.3). In Table 1 the reaction conditions for the preparation of Nd_2O_3 samples has been illustrated. For examining, the role of capping agent on the size and shape of Nd_2O_3 , one sample was formed without applying the capping agent. For evaluating the role of triethylenetetramine as a new precipitant, one sample was synthesized with employing ethylenediamine.

2.3. Photocatalytic measurements

The photocatalytic activities of as-synthesized Nd_2O_3 samples have been determined with employing the methylene blue contaminant solution. The reaction mixture comprising the 2 mg of the methylene blue contaminant and 80 mg of Nd_2O_3 samples in the glass reactor was employed to determine the

photocatalytic performance. After aerating for 1/2 h in darkness to obtain the adsorption–desorption equilibrium, the above mixture was subjected to the UV illumination from the 125 W mercury lamps. The methylene blue contaminant photodegradation efficiency has been determined as follow:

$$D.P.(t) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A_0 and A_t are the absorbance quantity of methylene blue contaminant solution before and after decomposition with a UV–vis spectrometer.

3. Results and discussion

XRD patterns of the sample no. 3 before and after calcination at 700 °C are presented in Fig. 1a and b, respectively. The diffraction peaks depicted in Fig. 1a and b may be readily ascribed to pure hexagonal phase neodymium hydroxide (JCPDS card 83-2035) and hexagonal phase neodymium oxide (JCPDS card 74-2139), respectively. The mean crystallite size of Nd_2O_3 sample determined with Scherrer formula [17] is about 35 nm.

Fig. 2a depicts FT-IR spectrum of Nd_2O_3 sample prepared by SDBS and triethylenetetramine. The peaks around 1047 and 1335 cm^{-1} may be ascribed to carbonate group [33]. The peak around 3459 cm^{-1} is corresponding to the $\nu(\text{OH})$ stretching vibration of physisorbed water. The peak nearly 650 cm^{-1} is due to neodymium oxide [34].

EDS pattern of Nd_2O_3 sample produced by SDBS and triethylenetetramine is presented in Fig. 2b. This figure reveals the presence of Nd and O elements in the as-formed sample. Based on the XRD, EDS and FTIR results, it is found that the pure hexagonal phase neodymium hydroxide nanostructures may be produced via the present precipitation route.

As mentioned before, in this investigation, Nd_2O_3 has been produced via a simple precipitation way. For the first time, Nd_2O_3 was formed with utilizing triethylenetetramine as a new precipitant and neodymium nitrate as a neodymium source. To examine the role of the kind of capping agent on the size and shape of Nd_2O_3 , several capping agents such as Titriplex, bis-(2-hydroxy-1-naphthaldehyde)-propandiamine and SDBS have been utilized. FESEM images of Nd_2O_3 samples formed with utilizing Schiff base, Titriplex and SDBS are depicted in Fig. 3a-f, respectively. It can be seen that irregular nano plates/ non-uniform micro/nano bundles (sample no. 1), less uniform nano bundles (sample no. 2) and uniform spherical Nd_2O_3 nanoparticles (sample no. 3) are produced with utilizing Schiff base, Titriplex and SDBS, respectively. SDBS creates the greatest steric hindrance influence compared with Titriplex and Schiff base. SDBS may play as the finest capping agent and impede the extra aggregation of primary nanoparticles and accordingly control growth of Nd_2O_3 . By enhancing steric hindrance influence, the grain size diminished, as presented in Fig. 3a-f. Based on the FESEM results, SDBS is the finest kind of capping agent for producing uniform spherical Nd_2O_3 nanoparticles with fine size (Fig. 3a-f).

For evaluating the capping agent role on the size and shape of Nd_2O_3 , one sample was formed without applying the capping agent. The irregular microstructures with large size are produced without applying the capping agent, as presented in Fig. 4a. Thus, utilizing capping agent has a substantial impact on the shape and size control of Nd_2O_3 .

For examining the role of the new precipitant (triethylenetetramine) on the shape and size of the Nd_2O_3 , one sample was formed with employing ethylenediamine. It can be seen that with employing ethylenediamine, high agglomerated microstructures/bulk structures are synthesized (Fig. 4b). The precipitant (triethylenetetramine) with the great steric hindrance influence may play as co-capping agent role via impeding the extra aggregation of primary nanoparticles. Based on the FESEM results, it is

found that utilizing SDBS and triethylenetetramine causes uniform spherical Nd₂O₃ nanoparticles with fine size (Fig. 3e and f).

TEM images of Nd₂O₃ product formed with utilizing SDBS and triethylenetetramine are presented in Fig. 5a-f. Diameters of formed Nd₂O₃ nanoparticles are nearly 10–40 nm.

The peak nearly 356 nm (Fig. 6a) appears in the DR-UV-vis spectrum of Nd₂O₃ sample formed with utilizing SDBS and triethylenetetramine. The energy gap (E_g) as substantial parameter in the photocatalytic efficiency has been calculated utilizing Tauc's equation and DR-UV-vis data [19]. The E_g quantity of Nd₂O₃ product (Fig. 6b) has been estimated from extrapolation of the plot of $(\alpha h\nu)^2$ against $h\nu$. The quantity of Nd₂O₃ sample formed with utilizing SDBS and triethylenetetramine was determined to be 3.33 eV. The estimated energy gap quantity indicates that Nd₂O₃ sample may be employed as photocatalyst under ultraviolet light.

The photocatalytic behaviors of Nd₂O₃ products synthesized with utilizing SDBS (sample no. 3) and Titriplex (sample no. 2) as well as without applying capping agent (sample no. 4) have been compared under ultraviolet light (Fig. 7). The photocatalytic efficiency of sample no. 3 with finer grain size is obviously more than other Nd₂O₃ structures, as illustrated in Fig. 7. From photocatalytic calculations, the methylene blue contaminant degradation was about 89.6 % by sample no. 3, 78.1 % by sample no. 2 and 53.2 % by sample no. 4 after 1.5 h ultraviolet illumination. The suggested mechanism of the decomposition of organic contaminant may be assumed as:

Table 2 presents the surface properties of Nd₂O₃ product synthesized with utilizing SDBS. Fig. 8a and b exhibits the nitrogen adsorption/desorption isotherm and pore size distribution of Nd₂O₃ product synthesized with utilizing SDBS, respectively. The distribution of the pores is multi-peak for the as-synthesized Nd₂O₃ product, as depicted in Fig. 8b. It is generally accepted that photocatalytic efficiency mostly depends on the accessible active sites on photocatalyst surface, the diffusion of reactants and products, and hence the convenient distribution of the pore [35, 36]. It seems that the proportion of surface area to volume, attainable active sites on Nd₂O₃ surface as well as transference extent charge carrier improved with diminishing size of Nd₂O₃, and thereupon causing more photocatalytic efficiency [36]. Based on the photocatalytic activity results, it is found that utilizing SDBS causes uniform spherical Nd₂O₃ nanoparticles with more photocatalytic efficiency (Scheme 1).

4. Conclusions

Pure hexagonal Nd₂O₃ nanostructures were produced via a simple and cost-effective precipitation way. For the first time, nanostructured Nd₂O₃ was successfully synthesized with utilizing triethylenetetramine as a new precipitant and neodymium nitrate as a neodymium source. For examining the influence of various capping agents on the morphology, grain size and photocatalytic efficiency of Nd₂O₃, several experiments were performed. The results indicated that the kind of capping agent has substantial impact on the shape, grain size and photocatalytic efficiency of Nd₂O₃. The photocatalytic activity results reveal

that the nanostructured Nd_2O_3 synthesized with utilizing SDBS may be utilized as beneficial and desirable photocatalyst under ultraviolet light.

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Table 1. The synthesis conditions of Nd₂O₃ products synthesized in this study.

Sample No.	Precipitant type	Kind of capping agent	Figure of FESEM images
1	Triethylenetetramine	Schiff base	3a and b
2	Triethylenetetramine	Titriplex	3c and d
3	Triethylenetetramine	SDBS	3e and f
4	Triethylenetetramine	-	4a
5	Ethylenediamine	SDBS	4b

Table. 2 The surface properties of Nd₂O₃ product synthesized with utilizing SDBS.

BET area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore diameter (nm)
26.001	0.07	4.8

Figure Captions:

Figure 1. XRD patterns of the sample no. 3 before (a) and after (b) calcination at 700 °C.

Figure 2. FT-IR (a) and EDS (b) spectra of Nd₂O₃ sample prepared by SDBS and triethylenetetramine.

Figure 3. FESEM images of Nd₂O₃ samples formed with utilizing Schiff base (a and b), Titriplex (c and d) and SDBS (e and f).

Figure 4. FESEM images of Nd₂O₃ samples formed in absence of the capping agent (a) and triethylenetetramine (b).

Figure 5. TEM images of Nd₂O₃ product formed with utilizing SDBS and triethylenetetramine.

Figure 6. DR-UV-vis spectrum (a), plot to determine the band gap (b) of Nd₂O₃ sample formed with utilizing SDBS and triethylenetetramine.

Figure 7. Photocatalytic methylene blue contaminant degradation of the as-formed Nd₂O₃ (sample nos. 2, 3 and 4).

Figure 8. N₂ adsorption/desorption isotherm (a) and pore size distribution curve (b) of Nd₂O₃ sample formed with utilizing SDBS and triethylenetetramine.

Scheme 1. Schematic diagram of the synthesis of the nanostructured Nd₂O₃ for photodegradation of methylene blue contaminant under ultraviolet illumination.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Scheme 1.